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No. 189

METHOD FOR DIFFERENTIATING AND ESTIMATING UNBLEACHED SULPHITE AND SULPHATE PULPS IN PAPER

BY

R. E. LOFTON, Associate Physicist
M. F. MERRITT, Laboratory Assistant
Bureau of Standards

APRIL 4, 1921

PRICE, 5 CENTS

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A METHOD FOR DIFFERENTIATING AND ESTIMATING UNBLEACHED SULPHITE AND SULPHATE PULPS IN PAPER

By R. E. Lofton and M. F. Merritt

ABSTRACT

The purpose of this paper is to fill a need felt especially by paper chemists and analysts for a rapid and reliable method of distinguishing between and of making an approximately correct quantitative determination of mixtures of unbleached sulphite and sulphate pulps. This paper gives briefly the basic differences in the manufacture of the two pulps, and contains a concise review of the methods that have been recommended from time to time for distinguishing between unbleached sulphite and sulphate pulps. It gives the procedure followed in developing a new and comparatively rapid method for distinguishing between these pulps, and also gives some of the more important experiments carried out with various stains during this investigation. The method of preparing the new stain and the method of procedure for differentiating between unbleached sulphite and sulphate fibers is described in detail, and tables showing the results of quantitative microscopical analysis of mixtures of these fibers stained by the new method are given.

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I. INTRODUCTION

The purpose of this publication is to give a review of the various methods proposed for distinguishing between unbleached sulphite and sulphate fibers, and especially to describe the development and application of a new method for accomplishing this result.

That there is and has existed for some time a demand for a quick and certain method for differentiating between these two pulps is indicated by the various attempts that have been made from time to time to develop such a method. To be satisfactory, any method proposed must be practical as well as certain—that is, it must not require any expensive apparatus, or special experience, or tedious and lengthy manipulation—but it must be such as may be carried out in a few minutes time by any one ordinarily familiar with the microscopical examination of paper-making fibers.

Such a method would be of service to pulp manufacturers and jobbers, to manufacturers of sulphite and sulphate papers, and to the retailers and consumers of sulphite and sulphate papers in aiding them to determine whether they are getting what they desire. It is useless for a jobber or a consumer to specifically order an all or part sulphate wrapping paper unless there is some means of determining whether the article ordered is being furnished.

The authors acknowledge the assistance of M. B. Shaw, who made a large number of fiber estimations, the results of which appear in Tables 3, 4, and 5, and who gave assistance as to methods of preparing the stains.

II. THEORETICAL CONSIDERATIONS INVOLVED

1. FUNDAMENTAL DIFFERENCES BETWEEN THE TWO PULPS

The difficulties to be overcome in developing a method for distinguishing between unbleached sulphite and sulphate pulps are due to the similarity of the pulps. Both are made, for the most part, from the same raw material, with but two or three exceptions. Spruce, hemlock, balsam fir, yellow pine, tamarack, and white fir are used in making both pulps. In addition to these woods, jack pine and cypress are often used in the sulphate process. Yellow pine is more generally used in the sulphate than in the sulphite process, because the former process is better adapted to woods rich in rosin and oil. The woods generally used in foreign countries are of the same kinds as those used in the United States and Canada except that black spruce is frequently used in Finland, Norway, and Sweden.

Since the raw material from which these pulps are made is in general the same, the only distinguishable differences between the pulps are to be found in the two different digesting processes employed in their manufacture.

Sulphite pulp is made by cooking wood chips in a solution of bisulphite of calcium, or of calcium and magnesium. This solution

has an acid reaction. The chips are cooked under a steam pressure of from 60 to 80 pounds for from 8 to 20 hours. The process was invented by B. C. Tilghman, of Philadelphia, who took out the first United States patent in 1867.

Sulphate pulp, frequently called "Kraft" (a German word meaning "strength"), is made by cooking wood chips in a solution the chief ingredient of which is sodium sulphide. The sodium "sulphate" added from time to time is reduced to "sulphide" during the preparation of the cooking liquor. The reaction of this solution is alkaline. In this process the chips are cooked under a steam pressure of about 100 pounds for from 2 to 7 hours. This process was invented by Carl F. Dahl, of Danzig, Germany, about 1883, and was introduced into America in 1907, when the Brompton Pulp and Paper Co. set up a sulphate mill in Canada.

Unbleached sulphite pulp is used in the manufacture of wrapping paper and bag stock, of many so-called Kraft and manila papers, of twines used in tying bundles and in making paper rugs, onion and potato sacks, and in any pulp or paper product where strength is the chief consideration. Sulphate pulp has a considerably darker color than sulphite, for which reason the latter is often colored in the process of being made into paper to resemble sulphate pulp. In general, sulphate pulp may be used wherever it is permissible to use unbleached sulphite. In cases where the greatest possible strength is required, sulphate is used instead of sulphite, since it is somewhat stronger. The cost of sulphate, due to a more expensive process of manufacture, is somewhat more than that of sulphite pulp.

2. POSSIBLE BASES OF DIFFERENTIATION

Commenting on the problem, C. W. Schwalbe stated[1] in 1914 that there was no simple method known at that time for distinguishing between unbleached sulphite and sulphate pulps; also, that it is difficult to develop such a method because the pulps are so closely related. Schwalbe recognized, too, as do others who have made a study of the two pulps, that there are two differences between them which may be used as a basis on which to develop reactions which will differentiate them, namely, (1) the difference in the amounts of incrusting or ligneous material, and (2) the different chemical changes which have been brought about by the different digesting processes.

[1] Testing Methods for Sulphite and Sulphate Cellulose in Paper, Pulp and Paper Magazine, p. 21; Jan. 1, 1914.

3. DIFFERENT AFFINITIES OF PULPS FOR DYES

It is pretty generally known by persons who have made any analytic study at all of paper-making pulps that those pulps differing in the degree of cooking, or of bleaching, or both, usually have quite different affinities for various dyes and stains. The dye most generally used to show the properties of different pulps in this respect is malachite green, a basic aniline or coal-tar dye which has a great affinity for highly lignified fibers and very little or no affinity for pulps and fibers freed from incrusting matter. The result of this property is that, when malachite green alone is used to stain a pulp composed of a mixture of fibers having a high content of lignin and of other fibers more thoroughly digested, one gets a range of shades varying from deep green to very light green, or, perhaps, to the entire absence of color in the case of fibers that are completely freed from incrusting matter. Although there may be no sharp color line of demarcation to set off any one group of fibers against any other, results of this kind may serve the purpose of determining the thoroughness or the uniformity of the cooking or of the bleaching action. But if this or a similar dye or stain is followed by one of a contrasting color, as recommended by Siebert and Minor,[2] it will sometimes be found possible to separate quite distinctly a mixture of two different pulps, as, for example, a well-cooked from a slightly-cooked pulp, or a well-bleached from a poorly-bleached pulp, or a chemical from a mechanical pulp. These authors, however, recommend that malachite green be followed by an acid dye, while in the method described below both of the dyes used are basic.

Whether the different affinities of the two pulps for various dyes and stains are due to different chemical properties of the pulps brought about by the different cooking methods, or whether they are due merely to the different amounts of incrusting matter remaining in the sulphite and sulphate pulps, is a question on which cellulose chemists do not agree.

III. METHODS PROPOSED BY EARLIER EXPERIMENTERS

In studying this problem the available methods proposed from time to time by others who have experimented along this line were tried. Below is given a description of each method, together with a brief statement of results obtained by the writers in trying the method.

[2] The Differentiation of Sulphite Pulps, Paper, 25, No. 21; Jan. 28, 1920.

1. KLEMM'S METHODS

Klemm is given credit for developing two methods, in one of which use is made of malachite green alone, and in the other use is made of both malachite green and rosaniline sulphate.

Klemm's malachite green method is described by R. W. Fannon [3] as follows:

> The reagent consists of a saturated solution of malachite green, a coal-tar dye, to which 2 per cent acetic acid has been added. A portion of pulp is treated with a few drops of the reagent sufficient to soak it, and the excess blotted up. The fiber is then examined microscopically. Unbleached sulphite is colored full green; sulphate is colored light green.

The results obtained by using this method were not satisfactory, since there is no sharp or distinct line of demarcation between the two pulps, some of the more deeply colored sulphate fibers showing a deeper green than some of the lighter colored sulphite fibers. These results are in harmony with the statements made above regarding the use of malachite green in staining various pulps and fibers.

Schwalbe mentions another procedure,[4] a malachite green and rosaniline-sulphate method, which he also calls Klemm's method. No details as to making up the dye solutions or method of applying them are given.

It was found, however, that a fairly good differentiation between the two pulps is had if they are stained for about two minutes with a one-half per cent aqueous solution of malachite green, rinsed with water, then stained with a solution of rosaniline sulphate acidified with sulphuric acid. The same results may also be obtained if these two stains are compounded in the right proportions before being applied to the pulps.

When the chemical composition of rosaniline sulphate is compared with that of magenta, or fuchsine, one of the dyes recommended below, it is evident that they are very closely related, and that the color radical is the same in both. An insight into the constitution of these compounds may be had from any good treatise on organic chemistry.

Pararosaniline and rosaniline [5] are the bases of the fuchsine dyes. Both are triacid bases, stronger than ammonia. The basic fuchsine or magenta dyes are formed by treating these bases with various acids, particularly hydrochloric and acetic,

[3] An effort to find a simple means of differentiation between sulphite and sulphate pulp. (A thesis prepared at the University of Maine, June, 1916.)

[4] Pulp and Paper Magazine, p. 21; Jan. 1, 1914.

[5] A. Bernthsen, Organic Chemistry, translation by J. J. Sudborough; New York, 1912.

water being eliminated during the reaction. The formula of rosaniline is

$$C(OH)\left\langle\begin{matrix}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_3(CH_3).NH_2\end{matrix}\right\rangle \text{ or } C_{20}H_{21}N_3O.$$

By treating with hydrochloric acid, the following reaction takes place:

$$\underset{\text{Rosaniline}}{C_{20}H_{21}N_3O} + \underset{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid}}}{HCl} = \underset{\substack{\text{Rosaniline}\\\text{hydrochloride}}}{C_{20}H_{20}N_3Cl} + \underset{\text{Water}}{H_2O}.$$

From analogy, it appears that a similar reaction takes place when rosaniline is treated with sulphuric acid, and that rosaniline sulphate is essentially a basic fuchsine or magenta dye, but with an acid radical not usually found in dyes put out under this name.

$$\underset{\text{Rosaniline}}{(C_{20}H_{21}N_3O)_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Rosaniline sul-}\\\text{phate}}}{(C_{20}H_{20}N_3)_2SO_4} + \underset{\text{Water}}{2H_2O}.$$

As the coloring power, however, of these dyes lies wholly in the basic constituent, there can be no doubt but that rosaniline sulphate is essentially basic fuchsine or magenta.

One authority [6] states that basic magenta is a mixture of the hydrochloride and acetate of rosaniline and pararosaniline; according to another, it is a mixture of the hydrochlorides of rosaniline and pararosaniline. The formula of pararosaniline is

$$C(OH)\left\langle\begin{matrix}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{matrix}\right\rangle \text{ or } C_{19}H_{19}N_3O.$$

The reaction of this base with acids is like that of rosaniline.

The malachite-green and rosaniline-sulphate stain, however, does not give as brilliant color contrast between the two kinds of fibers. This advantage of the use of basic fuchsine over that of rosaniline sulphate is probably explained by the greater solubility of basic magenta as compared with that of rosaniline sulphate, since it was found by test that basic magenta is much more soluble in water than is rosaniline sulphate. This fact is in harmony with the known properties of the salts of these acids.

[6] Thomas H. Norton artifical dyestuffs used in the United States, Special Agent Series, No. 121, Bureau Foreign and Domestic Commerce, Washington D. C. Ira Remsen, Organic Chemistry, Fifth revision; New York, 1909.

2. SCHWALBE'S METHODS

Schwalbe also describes[7] two methods of analysis, in one of which aqueous solutions of ferric chloride and potassium ferrocyanide are used, and in the other solutions of a copper salt and an organic dye. The former method is also briefly outlined by Fannon.[8]

The ferric-chloride and potassium-ferrocyanide method consists in extracting the pulps for about 30 minutes in alcohol and ether to remove rosin, treating with a 0.05 *N* solution of ferric chloride at from 60 to 80° C for about 30 minutes, or until all the fibers settle to the bottom of the container, washing with distilled water, and treating with a 1 per cent solution of sulphuric acid, to which is then added from four to eight drops of a 2 per cent solution of potassium ferrocyanide. The container and contents are then placed on a water bath and kept at a temperature of from 60 to 80° C for from 5 to 10 minutes. The pulps are then washed and examined under the microscope. Sulphite fibers are colored a deep blue, and sulphate fibers a much lighter blue.

This method did not give results that would enable a distinction to be made in all cases between the two pulps, nor to permit estimations in any case. Moreover, the process is too long and tedious to be practical. However, since Schwalbe so highly recommends this method, it is thought probable that better results could be obtained if enough time should be spent in studying and experimenting with it.

By the copper method the pulps are boiled in a solution of a copper salt such as copper sulphate, washed, then treated with a solution of an organic dye such as benzopurpurine 10B. The benzopurpurine treatment develops in some classes of fibers an intensely blue color, according to Schwalbe, due to the formation of a so-called copper lake with the copper salt retained by the fibers.

This method was not experimented with, since Schwalbe himself condemns it as being too involved and uncertain in results, especially with pulps so similar in their properties as unbleached sulphite and sulphate.

[7] Pulp and Paper Magazine, p. 21; Jan. 1, 1914.
[8] Thesis referred to above.

3. FANNON'S METHODS

Fannon [9] found that a saturated aqueous solution of rosaniline sulphate, to which is added 1 to 3 per cent of alcohol and enough sulhpuric acid to cause the solution to take on a violet shade, is a satisfactory stain. He used two methods of applying this stain and examining its staining action:

In the first method, two or three drops of the solution were allowed to fall in the same spot onto the samples of sulphite and sulphate pulps tested, and the color reactions observed with the unaided eye. The unbleached sulphite pulps showed "a deep bluish center with a yellow ring surrounding," while the sulphate sample gave "a deep red coloration." "From 7 to 15 minutes after the stain was dropped on, the distinctive colorings were evident. After an hour or so the colors faded."

In the second method, "mixtures of sulphate fibers and sulphite fibers were made, stained with the last-named solution. The different fibers developed their respective colorations, and under the microscope estimations of each were possible."

This stain was not found satisfactory when used according to either method recommended, because the color differences shown by the two pulps are not sharp enough to enable one to detect without doubt even the presence of small percentages of one pulp when mixed with the other.

IV. THE MALACHITE-GREEN AND FUCHSINE METHOD

1. SOURCES OF MATERIALS USED

The samples of pulps and papers used in this investigation consisted of 188 pieces collected from a number of different firms, and represent pulps manufactured in all parts of this country, and in at least four foreign countries, Canada, Finland, Norway, and Sweden. All possible information was obtained regarding these samples, such as the kind of wood used and in what locality grown, the degree of cooking, etc.

The dyes and stains used during the earlier part of this investigation were obtained chiefly from the chemical division of this Bureau. Most of them had been in stock for some time, and all, or nearly all, were of German manufacture. But after the method given below had been pretty thoroughly worked out, samples of the two dyes used in this method were obtained from different sources in this country in order to determine whether the different makes of dyes were equally suitable for the purpose.

[9] Thesis referred to above.

2. METHOD OF ATTACK AND EARLIER EXPERIMENTS

The method of conducting the investigation was to try out on the two kinds of pulps the reaction of various biological stains and dyes recommended by authorities on microscopical methods, and also other stains and dyes that were suggested in one way or another. Most of the experimenting was carried on with red, green, and blue dyes, since dyes of these colors are usually the most brilliant and positive in their coloring action. The few yellow dyes that were tried did not give sufficiently brilliant color effects on the fibers, and little work was done with them.

In making this investigation by what may be properly called the empirical method, a great number of tests were necessarily made that are relatively valueless and therefore are omitted from this publication. Those which may be of value to others who are experimenting along the same line are given in Table 1.

TABLE 1.—Interesting Experiments Made and Stains Used with the Color Reactions on Sulphate and Sulphite Fibers

[Ext. alc.=extracted with alcohol; aq.=aqueous; so'.=solution.]

Serial No.	How stained	Action on—		Remarks
		Sulphate	Sulphite	
2	Safranin in equal parts water and alcohol, rinsed with water, Delafield's hematoxylin.	Colorless to faint reddish brown.	Pink to light magenta.	Color difference quite noticeable.
6	Ext. alc., boiled 1 minute, ¼ per cent aq. sol. malachite green, rinsed with water, rosaniline sulphate and little sulphuric acid.	Clear blue, bundles green.	Pale gray to lavender.	Differentiation good.
7	Ext. alc., boiled 1 minute, ¼ per cent aq. sol. malachite green, rinsed with water, eosin in equal parts alcohol and water.	Dark blue.....	Colorless to faint purple.	Pits of sulphite fibers colored green.
13	Ext. alc., heated to 100°C in ¼ per cent aq. sol. malachite green, rinsed with water, 1 per cent aq. alc. sol. safranin.	Light to dark red.	Light to dark red.	Do.
17	Boiled 1 minute in 1 part rosaniline sulphate sol., then 1 part 1 per cent aq. sol. malachite green added, lightly rinsed with water.	Blue.....	Purple.....	Good differentiation.
44	Ext. alc., boiled in water, acidified solution 50 per cent alcohol, Delafield's hematoxylin 10 to 15 minutes, rinsed with water, ½ per cent sol. congo red 1 minute, rinsed with water.	Red.....	.....do.....	Fair differentiation.
45	Ext. alc., boiled in water, acidified solution 50 per cent alcohol, Delafield's hematoxylin left on until air dry, rinsed with water, ½ per cent sol. congo red 1 minute, rinsed with water.	.....do.....	Purple with little red.	Do.

TABLE 1.—Interesting Experiments Made and Stains Used with the Color Reactions on Sulphate and Sulphite Fibers—Continued

Serial No.	How stained	Action on—		Remarks
		Sulphate	Sulphite	
57	Ext. alc., washed with 1 per cent aq. sol. tannic acid, then equal parts 1 per cent aq. solutions acid fuchsine and malachite green 3 minutes, rinsed with water.	Blue	Purple	Good differentiation.
79	Ext. alc., boiled in water, dried with filter paper on slide, then 50 parts each of 1 per cent aq. solutions magenta and malachite green and 1 part 1 per cent aq. sol. tannic acid 2 minutes, quickly rinsed in 50–50 aq. alc. sol. slightly acidified with HCl, rinsed with water.	Greenish blue	do	Differentiation excellent.
82	Boiled in water, ½ per cent aq. sol. malachite green and aq. sol. rosaniline sulphate and little H_2SO_4, all left on fibers 2 minutes, then rinsed with water.	Blue	do	Color difference not as decisive as when magenta is used in place of rosaniline sulphate.
84	Slide as made up by No. 79 examined under microscope in polarized light, with both parallel and crossed nicols.	Various colors	Various colors.	No distinguishing properties appeared.
85	Boiled in water, pulped and examined under microscope in polarized light with both parallel and crossed nicols.	Yellow, orange, and blue.	Yellow, orange, and blue.	Do.

Some of the pulps were extracted with alcohol to remove resins, and this fact is indicated in each case in the table. The pulps were then rinsed and cooked, at first, in clear water, and pulped, no chemical being used in the cooking process, as it was thought that any chemical treatment might possibly interfere with the staining action to follow. Experiments that were conducted later, however, indicated that cooking the sample of paper in a one-half per cent aqueous solution of caustic soda does not have any effect on the action of the dyes. The alcohol used at various times and for various purposes, as indicated, was in all cases ethyl alcohol. The color appearances and other characteristics noted are those which appeared under the microscope.

3. DETAILED METHOD OF USING

The stain which was found to be most satisfactory in differentiating between unbleached sulphite and sulphate pulps or fibers was a mixture of one part of a 2 per cent aqueous solution of malachite green and two parts of a 1 per cent aqueous solution of

basic fuchsine, or magenta. The solutions were made up according to the following formulas, kept in tightly stoppered separate bottles, and mixed only when wanted for use:

A—Malachite green	2 g
Distilled water	100 cm^3
B—Basic fuchsine	1 g
Distilled water	100 cm^3

Since there is considerable variation in the quality of dyes from various sources, it is not to be expected that any given combination of dyes or method of procedure will best fit all cases; it is, indeed, more than probable that the compound stain will have to be modified somewhat as to its two components, depending on the source of the dyes.

After this stain, therefore, has been made up according to formula, it will be necessary to test it out on samples of sulphite and sulphate fibers. To do this, samples of unbleached sulphite and sulphate pulps should be prepared and a few fibers of each placed on a slide, care being taken not to get the two samples mixed. The fibers are then dried and stained, as directed below, and then examined under the microscope. All the sulphate fibers should have a blue or blue-green color, and all the sulphite fibers should have a purple or lavender color. If any purple fibers appear in the sulphate pulp this indicates that too much fuchsine is present in the combination, and a little more malachite green solution must be added to counteract this effect. If, on the other hand, some of the sulphite fibers show green or blue, there is too much malachite green in the combination, and more fuchsine solution must be added. Of course the analyst must be sure that he is using authentic samples of the two pulps for this test. When tested out in this manner and the proper combination found, the stain is ready to be used on unknown combinations of fibers containing either unbleached sulphite or sulphate, or both.

A mixture of one-half sulphite and one-half sulphate may also be used to test out the stain, the proper combination for the stain being indicated when one-half of the fibers are colored blue, and the other half purple.

The stain should not be used for more than a few hours after being compounded and should be made up anew at least each day.

The method of preparing the samples of pulps or papers for staining, and of applying the stain, is as follows:

The sample is boiled for a few minutes in water or in a one-half per cent aqueous solution of sodium hydroxide, and the fibers are thoroughly disintegrated by shaking in a test tube or other receptacle about half filled with water, glass beads being added if the fibers can not otherwise be separated. Several fibers are then removed by means of a teasing needle, or preferably by means of a glass tube [10] about seven thirty-seconds of an inch in diameter, placed on a microscope slide, and dried by the use of hard filter or blotting paper. Two or three drops of the compound stain are then placed on the fibers by means of a suitable dropper or a pipette and allowed to remain 2 minutes, during which time the fibers are being teased apart and moved about in the stain on the slide. This teasing is necessary in order that the stain may have equal opportunity to act on all the fibers. At the end of 2 minutes the excess stain is removed with three or four thicknesses of hard filter paper, and the fibers treated with three or four drops of a weak aqueous solution of hydrochloric acid, made by adding 1 cm^3 of concentrated acid (sp. gr. 1.19; HCl 37 per cent) to 1 liter of distilled water. The acid solution is allowed to remain on the slide for from 10 to 30 seconds, during which time the fibers are teased and moved about rapidly. Following this, the excess acid solution is removed with filter paper, three or four drops of distilled water applied, the fibers quickly teased about, and the water absorbed with filter paper. If all the excess stain has been removed from the slide at this point, a drop or two of water may be added, the fibers spread about on the slide, and a cover glass placed over them. But if too much stain remains on the slide at this point, it will be necessary to rinse again with distilled water before applying the cover glass. After the cover glass has been placed in position the fibers are ready for examination under the microscope.

4. ESTIMATING PERCENTAGES

The color contrast not only enables one to detect the presence of one or both of these fibers, but is sharp enough to enable one, after some practice, to make an approximately correct estimate of the percentages of each of these fibers present.

[10] F. C. Clark, Paper Testing Methods, Tappi Publishing Corp., New York, N. Y.; 1920.

In order to get a practical idea as to what could be accomplished in estimating the percentages of sulphite and sulphate fibers when stained as directed, three persons, all of whom had had experience in estimating the percentages of fibers stained with the zinc-chloride and iodine stain, made a number of estimations on known mixtures of these two pulps.

Seven mixtures, made from representative samples of sulphite and sulphate pulps, were prepared by weighing on a chemical balance the proper proportions of each pulp, the weights of the two components totaling 30 g in each case. The pulps were then thoroughly mixed by agitating in a tight container with considerable water. The series made up contained 20, 25, 40, 50, 60, 75, and 80 per cent of unbleached sulphite. A representative portion of each member of this series was placed in a container and labeled. Microscope slides were then made up from each of the seven samples, each slide being given an unknown mark of identification, and handed over to the analysts for their estimations. Four different series of estimates were made, in each of which a different make of American dyes was used.

V. SUMMARY OF RESULTS

In the tables below are given the results of estimates on the seven fiber mixtures, each table showing the results obtained by using dyes from one of the four sources.

TABLE 2.—Results of Analyses, Using Dyes from First Source

Number of estimations	Observer	Percentage sulphite in mixture				Error of average	Probable error (r)	Huge error (u)
		Estimated			Actual			
		Maximum	Minimum	Average				
						Per cent	Per cent	Per cent
16	A	40	20	23.8	20	+3.8	5.1	12.3
14	C	50	10	27.9	20	+7.9	8.8	21.6
16	A	50	20	33.1	25	+8.1	8.2	20.0
14	C	50	20	33.9	25	+8.9	8.7	21.2
16	A	60	25	41.6	40	+1.6	7.1	17.3
14	C	90	25	50.7	40	+10.7	12.7	30.9
16	A	75	40	51.6	50	+1.6	5.4	13.2
14	C	80	40	57.1	50	+7.1	9.5	23.1
16	A	80	60	67.2	60	+7.2	7.1	17.3
14	C	90	60	69.6	60	+9.6	8.7	21.2
16	A	90	25	73.7	75	−1.3	9.6	23.4
14	C	80	40	72.9	75	−2.1	7.8	18.9
16	A	95	75	80.6	80	+0.6	3.4	8.2
14	C	90	25	76.4	80	−3.6	10.1	24.7

TABLE 3.—Results of Analyses, Using Dyes from Second Source

Number of estimations	Observer	Percentage sulphite in mixture				Error of average	Probable error (r)	Huge error (u)
		Estimated			Actual			
		Maximum	Minimum	Average				
						Per cent	Per cent	Per cent
16	A	40	20	24.7	20	+4.7	6.0	14.7
2	B	25	25	25.0	20	+5.0	3.4	8.2
5	C	40	20	24.0	20	+4.0	6.0	14.7
16	A	50	20	37.2	25	+12.2	10.0	24.4
3	B	40	25	35.0	25	+10.0	8.3	20.2
5	C	25	20	24.0	25	−1.0	1.5	3.7
16	A	75	25	50.0	40	+10.0	10.5	25.5
3	B	60	50	53.3	40	+13.3	9.5	23.3
6	C	75	30	47.5	40	+7.5	10.8	26.3
16	A	75	50	54.1	50	+4.1	5.4	13.2
3	B	60	60	60.0	50	+10.0	6.7	16.5
6	C	60	40	51.7	50	+1.7	6.2	15.0
16	A	80	50	65.0	60	+5.0	7.6	18.6
3	B	75	50	66.7	60	+6.7	9.1	22.3
5	C	60	50	56.0	60	−4.0	4.3	10.4
16	A	80	60	75.6	75	+0.6	4.3	10.5
3	B	80	80	80.0	75	+5.0	3.4	8.2
5	C	80	70	77.0	75	+2.0	3.0	7.4
16	A	80	75	78.4	80	−1.6	1.9	4.6
3	B	80	75	78.3	80	−1.7	2.0	4.8
4	C	80	70	73.7	80	−6.3	5.1	12.4

TABLE 4.—Results of Analyses, Using Dyes from Third Source

Number of estimations	Observer	Percentage sulphite in mixture				Error of average	Probable error (r)	Huge error (u)
		Estimated			Actual			
		Maximum	Minimum	Average				
						Per cent	Per cent	Per cent
16	A	50	20	27.5	20	+ 7.5	8.8	21.4
16	B	40	20	26.9	20	+ 6.9	7.1	17.2
16	A	75	20	32.5	25	+ 7.5	10.6	25.8
16	B	50	20	37.2	25	+12.2	11.0	27.0
16	A	60	25	43.1	40	+ 3.1	8.0	19.5
16	B	75	25	48.4	40	+ 8.4	9.9	24.3
16	A	60	20	45.3	50	− 4.7	8.1	19.9
16	B	75	40	55.3	50	+ 5.3	7.6	18.5
16	A	75	25	55.0	60	− 5.0	8.0	19.5
16	B	80	40	63.8	60	+ 3.8	8.1	19.8
16	A	80	60	74.4	75	− 0.6	4.9	12.0
16	B	80	50	70.9	75	− 4.1	6.3	15.3
16	A	80	50	75.3	80	− 4.7	6.4	15.5
16	B	80	70	78.4	80	− 1.6	2.2	5.4

TABLE 5.—Results of Analyses, Using Dyes from Fourth Source

Number of estimations	Observer	Percentage sulphite in mixture				Error of average	Probable error (r)	Huge error (u)
		Estimated			Actual			
		Maximum	Minimum	Average				
						Per cent	Per cent	Per cent
17	A	25	20	20.6	20	+0.6	1.2	2.8
17	B	25	20	20.6	20	+0.6	1.2	2.8
17	A	40	20	28.2	25	+3.2	5.0	12.1
17	B	50	20	27.1	25	+2.1	4.8	11.8
17	A	60	25	40.6	40	+0.6	5.3	12.9
17	B	50	25	39.7	40	−0.3	3.0	7.2
17	A	60	10	48.8	50	−1.2	3.3	8.0
17	B	75	40	50.9	50	+0.9	5.5	13.4
17	A	75	25	58.8	60	−1.2	7.7	18.7
17	B	75	50	59.4	60	−0.6	4.8	11.6
17	A	80	60	74.1	75	−0.9	4.7	11.5
17	B	80	60	74.1	75	−0.9	4.7	11.5
17	A	80	75	78.2	80	−1.8	2.0	4.9
17	B	80	75	78.5	80	−1.5	1.8	4.5

The analysts, or persons who made the estimations, are referred to as "A," "B," and "C."

The error of averages is the difference between the average of all estimations for that particular case and the actual percentage of sulphite in the mixture. The average result is computed from a number of estimations in most cases; the exact number of estimations in each case is given in the tables.

The most probable error is an error of such magnitude that a single estimation has an equal chance of being either within the error or outside of it. The given errors are computed by the method of least squares according to the formula

$$r = 0.6745\sqrt{\frac{\Sigma X^2}{n}},$$

in which r is the most probable error, X is the error of one estimation, ΣX^2 is the sum of the squares of all errors of n estimations, and n is the total number of estimations made on that particular mixture by the given analyst.

The huge error is an error of such magnitude that the chances are equal that 9 estimations out of 10 will be within the error, and only 1 in 10 greater than it. These results are computed by the method of least squares, according to the formula

$$u = 1.65\sqrt{\frac{\Sigma X^2}{n}}, \text{ or } u = 2.44r,$$

in which u is the huge error.

In no case did an individual analyst make more than one estimation on the same microscope slide or the same field of fibers.

It is noteworthy that the errors in the last series, or table, are much less than those in the first three series. This is no doubt due in large part to the differences between the dyes used in the first three series and those used in Table 5, since those used in the last series gave much more satisfactory color effects than those used in the first three series. This result is also certainly due in part to the greater familiarity and experience the analysts had with the stain at the time the last series was run.

There are at least two criticisms that may be offered against these estimations. The first is that the results given may not quite represent estimates on wholly unknown mixtures, since each analyst knew in what proportion each of the seven combinations in the series was made up; although, as stated above, each sample was marked in code so that the analyst could not know what combination was being examined. When a study of the individual estimates is made, it appears that this circumstance did have an appreciable influence on the estimates on the mixtures near either end of the series. But since 0 per cent and 100 per cent are limits in all mixtures, it seems probable that estimates on mixtures near these limits will always be more nearly correct than estimates on mixtures containing a higher percentage of the smaller constituent.

The second criticism is that it is not practical in most cases to make 16 or 18 different estimates on the same sample of pulp or paper. This criticism is valid, especially as applied to mill conditions; for the paper-mill chemist is usually too busy to give so much time to the study of one sample of pulp or paper. It is necessary, however, that anyone, whether novice or expert, doing work of this kind, shall become familiar by actual experience with the use and properties of any stain before reliable results in estimating percentages can be had. To get best results in estimating, it is also necessary that one keep constantly in practice, and refer often to standard or known mixtures, accurately made up, and kept always at hand. When the analyst becomes familiar with the characteristics and use of the stain described above, it is probable that estimates can be made by its use as quickly and with as much accuracy as with the zinc-chloride and iodine stain.

WASHINGTON, November 27, 1920.

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